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CONCENTRATION OF BROMIDE IONS IN SEAWATER BY ISOTOPIC EXCHANGE WITH MERCUROUS BROMIDE

By
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In a previous study it was reported that silver bromide can concentrate the radioactive bromide ions in seawater by a process of isotopic exchange. Mercurous bromide looked more favorable because of its lower solubility and lower cost and it was thus used to determine its effectiveness, relative to silver bromide, in concentrating bromide ions from seawater. The effect of the height of the mercurous bed, flow rate and volume (residence time) of the seawater on the amount of bromide ions exchanged was studied. Each of the variables was found to have a significant effect. The results indicated that under the same conditions mercurous bromide can concentrate the bromide ion in seawater slightly more than the silver bromide.

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Concentration Of Bromide Ions In Seawater By Isotopic Exchange With Mercurous Bromide

There is a need for determining radioactive bromide ions in the ocean. The amount of bromine in seawater is relatively small (65 mg/l), and a substantial improvement in radioactive bromine detection sensitivity could be achieved by concentration of the bromine. A fast-reacting in-situ system is required for concentration of the bromine from large volumes of seawater.

In a previous study it was reported that silver bromide can concentrate the radioactive bromide ions in seawater by a process of isotopic exchange to permit counting of any radioactive bromine atoms present. Mercurous bromide looked more favorable than silver bromide because of its lower solubility and lower cost, and it was used to determine its effectiveness, relative to silver bromide, in concentrating bromide ions from seawater. The results indicated that under the same conditions mercurous bromide can concentrate the bromide ions slightly more than the silver bromide.

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ROBERT WILLIAMSON II
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

A method was required for the in-situ determination of radioactive bromide ions in seawater. The amount of radioactive bromide ions is expected to be very low and thus sensitive methods of analysis are sought. A substantial improvement in sensitivity could be achieved if the radioactive bromide ions in the seawater could be concentrated and then counted.

In a previous study[(1)] it was reported that silver bromide, AgBr, can concentrate the bromide ions in seawater by a process of isotopic exchange and that the seawater can desorb the bromide ions from AgBr. Another compound, mercurous bromide, Hg_2Br_2, looked more favorable because of its lower solubility and lower cost and was studied to determine its effectiveness, relative to AgBr, in concentrating bromide ions under similar conditions.

APPROACH

Seawater samples with ^{82}Br activity were passed through a column that contained the isotopic exchanger, Hg_2Br_2. The amount of ^{82}Br exchanged was determined by gamma counting aliquots of the sample before and after passage through the Hg_2Br_2 bed.

A 3 x 3 x 3 factorial experiment was set up to get a better study of the effect of the variables on the amount of ^{82}Br exchanged. The factorial experiment is useful in determining whether or not variations due to factors studied are greater than might be expected from purely random variations, and also in determining whether or not interactions between pairs of factors are significant. The factors studied in this experiment were the following: (1) height of the Hg_2Br_2 bed in the column, (2) flow-rate, and (3) volume (residence time, which is the time duration of flow).

In addition to the factorial experiment, the desorption rate of ^{82}Br from Hg_2Br_2 column was studied.

EXPERIMENTAL

MATERIALS

1. Mercurous bromide (Reliable Chemical Co.). The mercurous bromide was crushed and sieved through a Tyler standard screen. A 12-24 mesh screen (701-1397 microns) was used.

2. Synthetic seawater. Synthetic seawater is made by dissolving simulated sea salt mix, (Lake Product Co. Inc., St. Louis, Mo.) in distilled water. Simulated sea salt mix contains those elements found in natural sea salt in quantities greater than 0.004%.

3. Radioactive bromine. ^{82}Br was obtained by thermal neutron activation of ammonium bromide. A stock solution was made by dissolving the irradiated ammonium bromide in distilled water. An aliquot of the stock solution was added to synthetic sea water and stored in a polyethylene bottle.

APPARATUS

1. Exchange columns. Three columns were made, each consisting of a Pyrex tube (0.77 cm i.d.) with a glass frit on the bottom. A thin layer of glass wool was placed above the glass frit and the columns were each loaded with a water slurry of Hg_2Br_2 Column 1 was filled to a height of 1.5 cm, column 2 to a height of 4.5 cm and column 3 to a height of 13.5 cm. The dry weight of Hg_2Br_2 used for each column was 1, 3 and 9 g, respectively.

2. Vacuum pump. A Duo Seal pump was used to draw the seawater through the column into a suction flask attached to the bottom of the column.

3. Vacuum gage. In order to obtain reproducible flow rates, a gage which measures the vacuum in inches of mercury was used. Vacuum was adjusted by bleeding air into the system through a stopcock (see Figure 1).

4. Gamma ray counter. A 3 in. x 3 in. sodium iodide [NaI(Tl)] scintillation detector with a well was used. It was encased in a 3 in. thick lead shield.

PROCEDURE

Seawater ^{82}Br activity was passed through the columns containing Hg_2Br_2 at various flow rates. The percentage of the radioactive bromide ions retained by the Hg_2Br_2 was calculated by the equation:

$$\%\ \text{retention} = \frac{Br(B) - Br(A)}{Br(B)} \times 100$$

where:

$Br(B)$ = ^{82}Br activity in seawater before passage through Hg_2Br_2

$Br(A)$ = ^{82}Br activity in seawater after passage through Hg_2Br_2

A series of runs were made on each of three Hg_2Br_2 columns in accordance with the flow-rates and residence times shown in Table 1. The corresponding volume of seawater used in each run is also shown in Table 1. The apparatus used for these measurements in shown in Figure 1.

The rate of desorption of ^{82}Br from Hg_2Br_2 was also studied. For this study a 13.5 cm and a 1.5 cm Hg_2Br_2 bed with adsorbed ^{82}Br were each washed with four 10 ml aliquots of seawater which did not contain ^{82}Br. The four washings were passed through each column at a flow rate of 0.37 ml/cm^2 - sec in rapid succession. The percentage of the radioactive-bromide ions desorbed from the Hg_2Br_2 was calculated by the equation:

$$\% \text{ desorption} = \frac{Br(D)}{BR(O)} \times 100$$

where:

Br(D) = ^{82}Br activity desorbed from the Hg_2Br_2 bed with each seawater wash

BR(O) = ^{82}Br activity on the Hg_2Br_2 bed before the four seawater washings

RESULTS

A statistical analysis of the data was performed with the aid of a computer and are presented in Table 2. A description of the statistical treatment of the data obtained in a factorial experiment such as this may be found in standard texts on experimental statistics. For each of the three main factors; volume (A), flow rate (B) and amount of Hg_2Br_2 (C), a quasi F-ratio is computed in accordance with the approximation

$$F = \frac{MS(A)+MS(ABC)}{MS(AB)+MS(AC)}$$

that applies to a Model II (random effects) three-factor experimental design. Degrees of freedom for numerator and denominator are approximated by the Standard Satterthwaite formula. Replications of each experiment were not done and thus it was not possible to evaluate the random error; consequently, there is no check on the significance of a third-order interaction. The mean square for the third-order interaction is used in computing F-ratios for each of the second order interactions. Thus, the F-ratios for AB, AC and BC in Table 2 are the ratios of the "mean square" of the second order interaction to the "mean square" of the third order interaction (ABC). By comparing the F-ratios in Table 2 with the critical F value tabulated by Fisher and Yates(2) for tests of significance, it is seen that in the ranges studied the amount of Hg_2Br_2, flow-rate, residence time as well as the interactions between these factors all have significant effects on the isotopic exchange of ^{82}Br with Hg_2Br_2.

The observations in Table 1 are also presented in plotted form in Figure 2. From Figure 2, it can be seen that the isotopic exchange of ^{82}Br with Hg_2Br_2 increases with column height, decreases with flow rate, and, to a lesser extent, decreases with residence time.

The data obtained in the desorption study are presented in Table 3. Initially, the radioactive bromide ions are rapidly desorbed, but the rate of desorption diminishes with time.

CONCLUSION

The results when compared to those obtained for AgBr, as reported in reference (1), indicate that Hg_2Br_2 can concentrate the bromide ions slightly better than AgBr and the seawater can desorb the bromide ions from Hg_2Br_2 at a faster rate than from AgBr. The optimization of the concentration system would involve trade-offs between amounts of Hg_2Br_2 used, flow-rates and counting system.

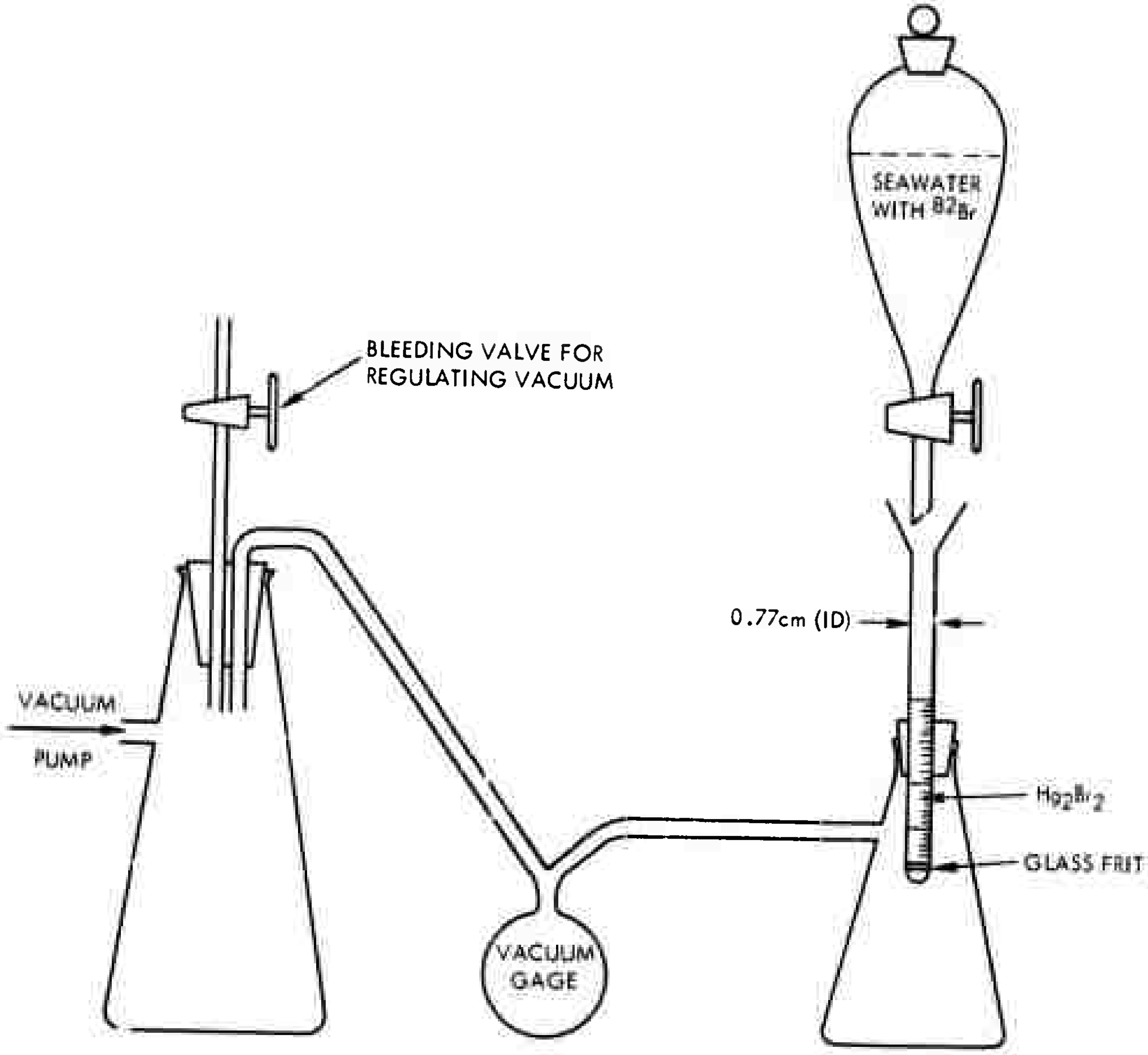

FIG. 1 APPARATUS USED FOR THE ISOTOPIC EXCHANGE

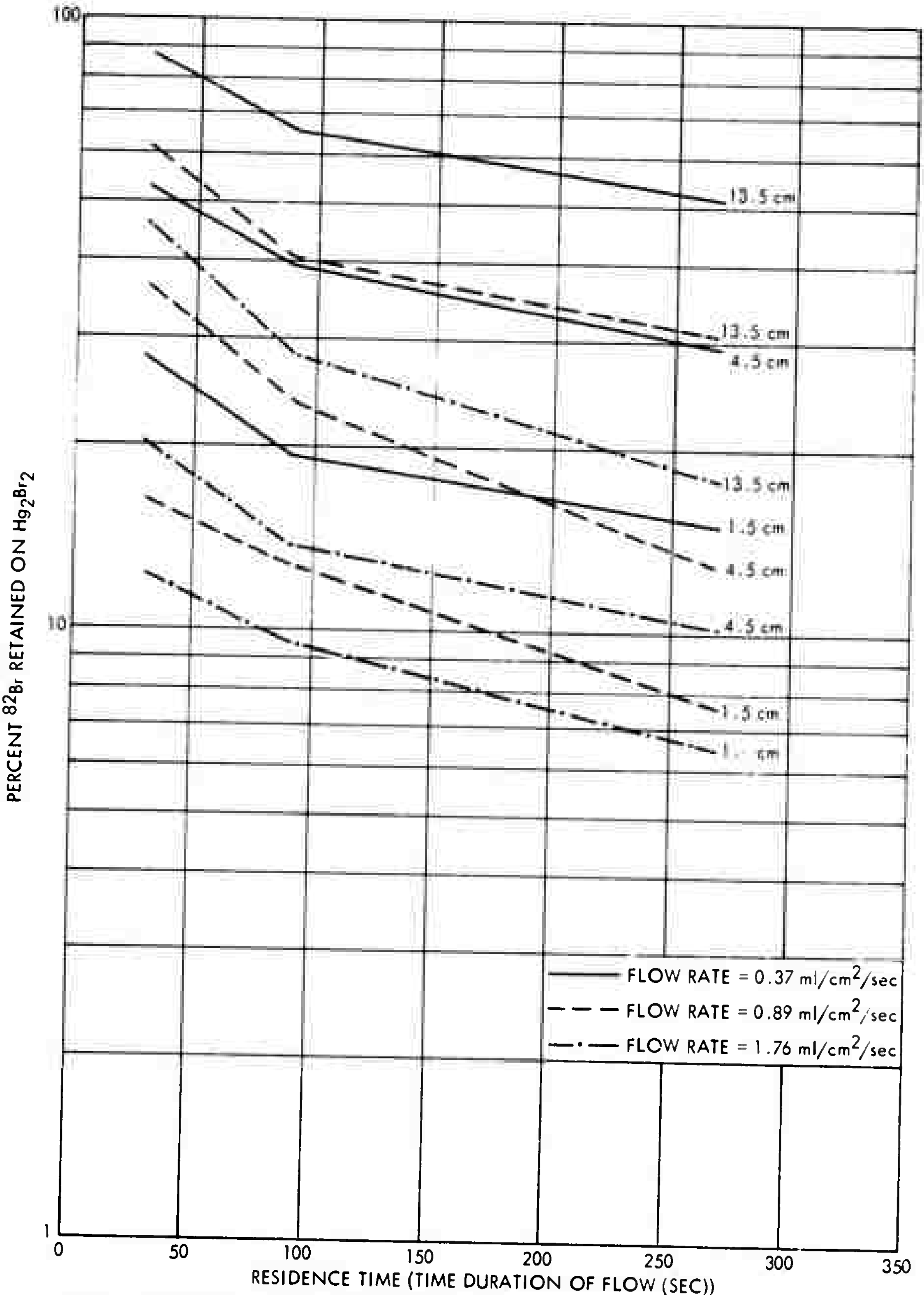

FIG. 2 RETENTION OF BROMIDE IONS BY ISOTOPIC EXCHANGE IN Hg_2Br_2 COLUMNS

TABLE 1

ISOTOPIC RETENTION OF ^{82}BR WITH MERCUROUS BROMIDE

Volume (ml)	Residence Time (sec)	Bromine Retention (%)		
		Col. 1 (1.5 cm)	Col. 2 (4.5 cm)	Col. 3 (13.5 cm)
Flow-rate = 0.37 ml/cm^2/sec				
5	30	27.8	52.4	86.3
15	90	19.4	39.5	65.3
48	270	15.0	29.2	50.8
Flow-rate = 0.89 ml/cm^2/sec				
13	30	16.4	36.6	61.7
39	90	12.8	23.9	40.6
115	270	7.6	13.0	30.9
Flow-rate = 1.76 ml/cm^2/sec				
25	30	12.4	20.2	45.7
72	90	9.5	13.8	28.8
245	270	6.5	10.3	17.7

TABLE 2

STATISTICAL ANALYSIS OF THE DATA

Factors	Degrees of Freedom	Sum of Square of Deviations (SS)	Mean Squares (MS)	F ratio
Single Factors				
Volume (A)	2	1791	895	7.9
Flow rate (B)	2	2783	1391	10.0
Hg_2Br_2 (C)	2	5124	2562	11.7
Interactions				
Volume x Flow rate (AB)	4	68	16.9	5
Volume x Hg_2Br_2 (AC)	4	388	96.9	32
Rate x Hg_2Br_2 (BC)	4	493	123	41
Volume x Flow rate x Hg_2Br_2 (ABC)	8	25.2	3.1	

TABLE 3

DESORPTION OF ^{82}Br FROM Hg_2Br_2

Seawater Washes (10 ml aliquots)	$^{82}Br^-$ Desorption % 9g	1g
First	24.7	55.3
Second	21.0	11.7
Third	9.0	5.2
Fourth	5.7	2.9
^{82}Br remaining on Hg_2Br_2 bed after 4 washes	40.2	25.6
TOTAL RECOVERY	99.6	100.7

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2. Fisher, R., and Yates, F., "Statistical Tables," Oliver and Boyd, London, 1938.